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Abstract

MISCIBILITY GAP IN EXTRACTION SYSTEMS INVOLVING ALKYLAMINES

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The formation of a third phase, a second organic one, is frequent in solvent extraction processes involving long-chain amines and aliphatic hydrocarbons as diluents. Quaternary systems (tertiary amine-diluent-water-hydrochloric acid) and quintanary systems, involving uranyl chloride, have been studied.

When solutions of amines in aliphatic hydrocarbons are equilibrated with equal volumes of aqueous hydrochloric acid of increasing concentration, there is a lower critical acid concentration at which the equilibrium organic phase splits into two, thus forming a third phase, and an upper critical acid concentration, which causes the third phase to disappear or prevents its formation. The "miscibility-immiscibility" of the two organic phases in equilibrium is reversible.

This phenomenon of a miscibility gap in a two-phase conjugate system is apparently unrelated to the dielectric constant or the dipole moment of the diluent, since in aromatic hydrocarbons the organic phase remains throughout homogeneous. Estimates based on the solubility parameter concept and expressed in terms of the Flory-Huggins entropy of mixing equation permitted quantitative differentiation between the aliphatic and aromatic hydrocarbon diluents, but failed to explain the differences observed among different aliphatic hydrocarbons. Calculations based on the molar polarizabilities, P_{12}, of the amine-diluent mixtures and expressed in terms of the Clausius-Mossotti equation, show a correlation between polarizability and miscibility, immiscibility being favoured by higher P_{12}.

Examination of the growth and diminution of the third phase in the system trinonylamine-hexane as a function of acid concentration, of the composition of the phases in equilibrium, and of their conductance, indicated that the third phase formation is accompanied by a chemical reaction leading to the formation of charged species.

An excess of HCl over and above the amount needed for the formation of the amine hydrochloride produces the splitting of the homogeneous organic phase; when the amount of acid transferred from the aqueous phase equals twice the total amine concentration, the organic phase becomes homogeneous again. The amine hydrogen dichloride is formed when the acid/amine ratio is higher than unity. The dichloride ion cannot be free but must exist in the organic solution in a tight ion-pair with the proton. The conductometric measurements suggest that indeed both the amine hydrochloride and the amine hydrogen dichloride are poorly conducting species, whereas charged species exist in the organic phase throughout the acidity range in which the miscibility gap exists. It is suggested that these charged species are formed through association of a single ion with the dipole of an ion-pair and are intermediate to the formation of amine hydrogen dichloride quadrupoles.

In aromatic hydrocarbons the amine hydrochloride is a solvent-shared or solvent-separated ion-pair, as distinguished from the state of the solute in the ideally non-solvating aliphatic hydrocarbons.